STRUCTURAL STUDIES OF SOME MICROBIAL POLYSACCHARIDES

A THESIS SUBMITTED BY

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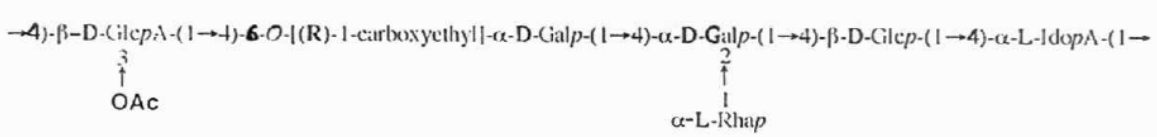
ABSTRACT

The thesis consists of seven chapters. The first chapter is a general introduction which includes a brief account of some degradative methods used for structural studies of polysaccharides.

The second chapter describes the general experimental conditions and the principal techniques used during the structural studies of microbial polysaccharides discussed in the next five chapters. Sugar analysis and methylation analysis combined with Gas Liquid Chromatography and Mass Spectroscopy (GLC-MS), were used for identification of components and for determination of the linkage positions in the repeating unit of the capsular polysaccharides. Location of substituents and sequential studies were carried out mainly by Nuclear Magnetic Resonance Spectroscopy (NOESY) and Fast Atom Bombardment Mass Spectroscopy (FAB-MS) studies of the oligosaccharides isolated from partial acid hydrolysates and specific degradations.

The extracellular polysaccharide from *Butyrivibrio fibrisolvens* strain X6C61 was found to have the hexasaccharide repeating unit shown in Structure 1.

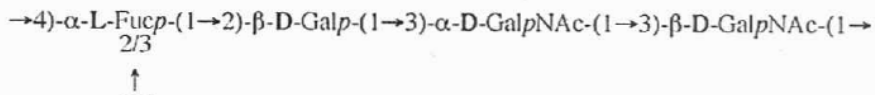


Structure 1

2D-NMR spectroscopy showed that the *O*-acetyl groups were located mainly on *O*-3 of the β-D-Glc*p*A residue.

The structure of the *B. fibrisolvens* strain X6C61 polysaccharide contains several unusual features. The repeating unit consists of three different acidic sugar residues. One of these, 6-*O*-[(R)-1-carboxyethyl]-D-galactose, has not been found previously in any naturally occurring substance .

The O-specific side-chain of the lipopolysaccharide from *Escherichia coli* O90 was found to have the tetrasaccharide repeating unit shown in Structure 2. The polysaccharide was found to contain approximately one mole of *O*-acetyl groups in the repeating unit. Periodate oxidation was used to determine the location of the *O*-acetyl groups. *E. coli* O90 strain possesses human blood-group activity and Structure 2 constitutes the blood-group H antigen.



Structure 2

Structural studies of another O-specific side-chain of the lipopolysaccharide from *Escherichia coli* O153 is discussed in the fifth chapter of the thesis. Smith degradation and FAB-MS experiments were used in this study. The linked-scan experiment of the permethylated oligosaccharides were used to determine the linkage

positions of the two amino sugar residues in the pentasaccharide repeating unit shown by Structure 3. Ribofuranosyl residues have not been found previously in the O-antigenic polysaccharides of enterotoxigenic *E. coli*.

→4)-β-D-Gal*p*-(1→4)-α-D-Glc*p*NAc-(1→4)-β-D-Gal*p*-(1→3)-α-D-Gal*p*NAc-(1→2)-β-D-Rib*f*-(1→

Structure 3

Chapter six describes a modified reaction sequence for the oxidative decarboxylation of glycouronans using lead tetraacetate. The reaction sequence was used to obtain evidence for the distribution of side chain residues in Welan gum (S-130) polysaccharide. Degraded polysaccharides were separated and analysed by FAB-MS. Fragments composed of fourteen sugar residues were isolated after the degradation. Informative fractions obtained from the degradation were trimers and dimers of the repeating units. FAB-MS analysis of these two fractions indicated that the distribution of the rhamnose and mannose in the side chain is random.

The last chapter of the thesis describes preliminary structural studies of the extracellular polysaccharide produced by the fungus *Colletotrichum capsici* isolated from the Sri Lankan fruits papaw and capsicum. The polysaccharide was composed of D-mannose, D-galactose, and D-glucose and the side chain of the

polysaccharide contained mainly mannose and glucose. Most of the galactose residues were branched at *O*-2 and *O*-6, and were in the furanose form. Glucosyl and mannosyl residues were α-linked and galactosyl residues had the β-anomeric configuration.